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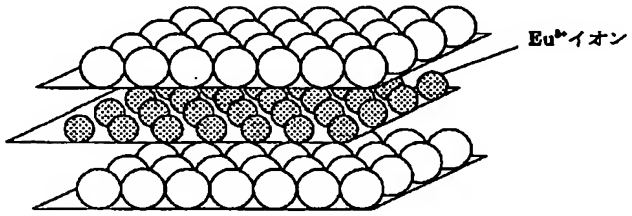
(54)【発明の名称】　赤色発光蛍光体及びそれを用いた発光装置

(57)【要約】
【課題】　長波長紫外線および短波長可視光線（３５０ｎｍから４２０ｎｍ）、特に波長３７０ｎｍ前後の励起光に対して赤色発光を効率よく放射でき、1個の発光ダイオードから白色ないし任意の色調を取り出すために実用的に使用できる赤色発光蛍光体およびその蛍光体を使用したＬＥＤランプを提供する。
【解決手段】　発光波長が３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線により励起され発光する蛍光体において、Eu^{3+}イオンを2次元または1次元に配列した蛍光体。



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【特許請求の範囲】

【請求項１】　発光波長が３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線により励起され発光する蛍光体において、Eu^{3+}イオンを２次元または１次元に配列した蛍光体であることを特徴とする赤色発光蛍光体。

【請求項２】　上記蛍光体の組成が、$AEu_XLn_{(1-X)}M_2O_8$で表されることを特徴とする請求項１記載の赤色発光蛍光体。但し，$0<x\leqq1$，組成中のＡはＬｉ，Ｎａ，Ｋ，Ｒｂ及びＣｓからなる群より選ばれた少なくとも１種であり，ＬｎはＹ，Ｌａ，Ｇｄ及びＬｕからなる群より選ばれた少なくとも１つであり，ＭはＷまたはＭｏからなる群より選ばれた少なくとも１１種である。

【請求項３】　$AEu_XLn_{(1-X)}M_2O_8$（但し，$0<x\leqq1$，組成中のＡはＬｉ，Ｎａ，Ｋ，Ｒｂ及びＣｓからなる群より選ばれた少なくとも１種であり，ＬｎはＹ，Ｌａ，Ｇｄ及びＬｕからなる群より選ばれた少なくとも１つであり，ＭはＷまたはＭｏからなる群より選ばれた少なくとも１種である）で表される組成を有する赤色発光蛍光体において、その粒子径が５０μｍ以下であることを特徴とする請求項２記載の赤色発光蛍光体。

【請求項４】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光チップ上に、上記請求項１乃至３の何れかに記載の蛍光体層を設けたことを特徴とする発光装置。

【請求項５】　上記蛍光体層が、請求項１又は２記載の蛍光体からなる複数の蛍光体層で構成されている請求項４記載の発光装置。

【請求項６】　上記蛍光体層が、請求項１又は２記載の複数の蛍光体を混合した単層構造である請求項４記載の発光装置。

【請求項７】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光ダイオードのモールド部材に、上記請求項１又は２に記載の蛍光体を分散させたことを特徴とする発光装置。

【請求項８】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光ダイオードのモールド部材に複数の蛍光体を分散させ，その蛍光体の１つに上記請求項１又は２に記載の蛍光体を用いたことを特徴とする発光装置。

【請求項９】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光ダイオードのモールド部材の外側に、請求項１又は２に記載の蛍光体層を設けたことを特徴とする発光装置。

【請求項１０】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光ダイオードのモールド部材の外側に、複数の発光層を設け，その発光層の１つが上記請求項１又は２に記載の蛍光体である発光

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装置

【請求項１１】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光ダイオードのモールド部材の外側に、複数の蛍光体を混合した混合層を設け，その蛍光体の１つに上記請求項１または２に記載の蛍光体を用いた発光装置。

【請求項１２】　赤色発光蛍光体として上記請求項１又は２に記載の蛍光体と、他の赤色発光蛍光体を少なくても1種混合することを特徴とする請求項４乃至１１の何れか１項に記載の発光装置。

【請求項１３】　３５０ｎｍから４２０ｎｍの長波長紫外線及び短波長可視光線を発光する発光ダイオードのモールド部材の外側に、複数の蛍光体を混合した被覆体を被せ、その蛍光体の１つに請求項１または２に記載の蛍光体を用いた発光装置

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、３５０ｎｍから４２０ｎｍの長波長紫外線および短波長可視光線により励起され赤色に発光する蛍光体及びその蛍光体を用いた発光装置に関する。

【０００２】

【従来の技術】現在、主に使用されている長波長紫外線および短波長可視光線（３５０ｎｍから４２０ｎｍ）で励起する蛍光体としては、発光色が青色の$BaMg_2Al_{16}O_{27}$：Ｅｕ，$(Sr, Ca, Ba)_5(PO_4)_3Cl$：Ｅｕ、緑色の$BaMg_2Al_{16}O_{27}$：Ｅｕ，Ｍｎ，Zn_2GeO_4：Ｍｎ、赤色のY_2O_2S：Ｅｕ、３．５ＭｇＯ・０．５MgF_2・GeO_2：Ｍｎがある。これら３色の蛍光体を任意の割合で混合することによって、長波長紫外線及び短波長可視光線で多くの発光色を作ることができる。しかし、白色系の場合、赤色成分のY_2O_2S：Ｅｕ蛍光体の発光効率が他の蛍光体よりもかなり低いために混合割合が多くなるといった問題があった。更に、白色系では赤、緑、青の発光バランスにより白色を得ることができるが、赤色成分の発光効率が悪いために緑、青系蛍光体の発光量を低く抑えなければならず、高輝度の白色が得られなかった。

【０００３】酸化物系化合物の電子対の励起エネルギーに対応する波長は紫外領域にあり、長波長紫外線および短波長可視光線（３５０ｎｍから４２０ｎｍ）は蛍光体の吸収端と重なる。この問題を解決するためユーロピウムで付活された希土類酸硫化物蛍光体が特開平１１－２４６８５７号公報や特開２０００－１４４１３０号公報で提案され、励起波長を長波長側へシフトすることが報告されている。しかし、３７０ｎｍ付近の紫外ＬＥＤの発光波長は、これら蛍光体の吸収端と重なるため紫外ＬＥＤの発光ピークのシフトにより発光量が著しく変化してしまう問題があった。

【０００４】一方、発光ダイオード（ＬＥＤ：Light E

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mitting Diode）は光を放射する半導体ダイオードであり、電気エネルギーを可視光または赤外光に変換するものである。特に可視光を利用するためにＧａＰやＧａＡｓＰ，ＧａＡｌＡｓ等の発光材料で形成した発光チップを透明樹脂等で封止したＬＥＤランプとして広く使用されている。また、発光材料をプリント基板や金属リードの上面に固定し、数字や文字を形どった樹脂ケースで封止したディスプレイ型のＬＥＤランプも多用されている。

【０００５】又、発光チップの表面乃至発光ダイオードの樹脂中に各種の蛍光体粉末を含有させることにより、放射光の色を適正に調整することも可能である。即ち、ＬＥＤランプの発光色は、青色から赤色まで各使用用途に応じた可視光領域の発光を再現することができる。また、発光ダイオードは半導体素子であるため、寿命が長く、信頼性も高く、光源として用いた場合には、その交換作業も軽減化されることから、携帯通信機器，パーソナルコンピュータ周辺機器，ＯＡ機器，家庭用電気機器，オーディオ機器，各種スイッチ，バックライト用光源，表示板等の各種表示装置の構成部品として広く使用されている。

【０００６】

【発明が解決しようとする課題】しかしながら、最近では、上記各種表示装置の利用者の色彩感覚が更に向上し、各種表示装置においても、微妙な色合いをより高精細に再現できる機能が要求されている。また、１個の発光ダイオードによって白色乃至各種の中間色を再現できる機能も強く求められている。

【０００７】そのため、ＬＥＤランプの発光チップの表面に、さらに青色，赤色，緑色発光蛍光体を塗布したり、発光ダイオードを構成する樹脂中（例えば、モールド部材、コーティング部材等）に上記各種蛍光体粉末を含有させることにより、１個の発光ダイオードから白色乃至任意の中間色を取り出すように構成することも試行されている。

【０００８】しかしながら、赤色発光蛍光体は、他の青色，緑色発光蛍光体と比較して長波長紫外線および短波長可視光線（３５０ｎｍから４２０ｎｍ）、特に波長３７０ｎｍ前後の励起光に対して吸収が弱いといった問題点があった。また、例えば赤色蛍光体Y_2O_2S：Ｅｕや特開平１１－２４６８５７号公報や特開２０００－１４４１３０号公報で提案されているユーロピウムで付活された希土類酸硫化物蛍光体の励起波長は、３５０ｎｍより長波長では急激に吸収強度が低下する。このことから３５０ｎｍ～３８０ｎｍを発光ピークとする励起光源、例えば紫外ＬＥＤを励起光源に用いた場合、紫外ＬＥＤ製造上で発生する発光ピークのシフトにより蛍光体の赤色発光量が著しく変化し、微妙な色合いをより高精細に再現することが難しい。

【０００９】本発明は、上記問題点を解決するためにな

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されたものであり、長波長紫外線および短波長可視光線（３５０ｎｍから４２０ｎｍ）、特に波長３７０ｎｍ前後の励起光に対して赤色発光を効率よく放射でき、１個の発光ダイオードから白色ないし任意の色調を取り出すために実用的に使用できる赤色発光蛍光体およびその蛍光体を使用したＬＥＤランプを提供することを目的とする。

【００１０】

【課題を解決するための手段】本発明者らは、上記目的を達成するため、種々の組成からなる赤色発光蛍光体を調製し、この組成成分の種類および添加量が蛍光体の励起スペクトル分布および発光強度に及ぼす影響を実験により比較検討した。

【００１１】その結果、ユーロピウムが低次元に配列した化合物、例えば$LiEuW_2O_8$において長波長紫外線および短波長可視光線（３５０ｎｍから４２０ｎｍ）、特に波長３７０ｎｍ前後の励起光を吸収し、赤色発光を効率よく放射できることが可能な赤色発光蛍光体が得られることを明らかにした。本発明は上記知見に基づいて完成されたものである。

【００１２】即ち、本発明に係る赤色発光蛍光体は、Eu^{3+}イオンが２次元または１次元に配列した蛍光体であることを特徴とする。Eu^{3+}イオンが2次元に配列した状態とは、図６に示すようにEu^{3+}イオンが同一平面内において縦・横方向に配列されている状態をいい、１次元に配列した状態とは図７に示すようにEu^{3+}イオンが同一平面内において縦方向（又は横方向）に配列されている状態をいう。

【００１３】更に、組成が$AEu_XLn_{(1-X)}M_2O_8$（但し、$0<x\leqq1$、組成中のＡはＬｉ，Ｎａ，Ｋ，ＲｂおよびＣｓからなる群より選ばれた少なくとも１種であり、ＬｎはＹ，Ｌａ，ＧｄおよびＬｕからなる群より選ばれた少なくとも１つであり、ＭはＷ又はＭｏからなる群より選ばれた少なくとも1種である。）で表されることを特徴とする。また、最も好ましい組成は$LiEuW_2O_8$である。

【００１４】又、本発明に係る赤色発光蛍光体は、$AEu_XLn_{(1-X)}M_2O_8$（但し，$0<x\leqq1$、組成中のＡはＬｉ，Ｎａ，Ｋ，ＲｂおよびＣｓからなる群より選ばれた少なくとも1種であり、ＬｎはＹ，Ｌａ，ＧｄおよびＬｕからなる群より選ばれた少なくとも１つであり、ＭはＷまたはＭｏからなる群より選ばれた少なくとも１種である）の組成であり、その粒子の平均粒子径が５０μｍ以下であることを特徴とする。

【００１５】さらに、本発明に係る発光装置は蛍光体と組み合わされた発光チップに通電することにより電気エネルギーを可視光または赤外光に変換するＬＥＤにおいて、上記発光チップ上に設けられた蛍光体層が$AEu_XLn_{(1-X)}M_2O_8$（但し、$0<x\leqq1$、組成中のＡはＬｉ，Ｎａ，Ｋ，ＲｂおよびＣｓからなる群より選ば

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れた少なくとも1種であり、LnはY，La，Gdおよびルからなる群より選ばれた少なくとも1つであり、MはWまたはMoからなる群より選ばれた少なくとも1種である）であることを特徴とする。ここで、発光チップ上に設ける上記蛍光体層は、少なくても1種以上の蛍光体を単層又は複数層を層状に積層配置しても良いし、複数の蛍光体を単一の層内に混合して配置しても良い。上記発光チップ上に蛍光体層を設ける形態としては、発光チップの表面を被覆するコーティング部材に蛍光体を混合する形態、モールド部材に蛍光体を混合する形態、或いはモールド部材に被せる被覆体に蛍光体を混合する形態、更にはLEDランプの投光側前方に蛍光体を混合した透光可能なプレートを配置する形態等が挙げられる。

【0016】又、上記蛍光体は発光チップ上のモールド部材に少なくても1種以上の蛍光体を添加しても良い。更に、上記蛍光体の1種以上の蛍光体層を、発光ダイオードの外側に設けても良い。発光ダイオードの外側に設ける形態としては、発光ダイオードのモールド部材の外側表面に蛍光体を層状に塗布する形態、或いは蛍光体をゴム，樹脂，エラストマー等に分散させた成形体（例えば、キャップ状）を作成し、これをLEDに被覆する形態、又は前記成形体を平板状に加工し、これをLEDの前方に配置する形態等が挙げられる。

【0017】ここで、上記赤色発光蛍光体においてユーロピウムは励起光の吸収と発光中心として作用する。一般的な酸化物系蛍光体では電子対の励起エネルギーに対応する波長は紫外領域にある。母体結晶により励起光を吸収し、その励起エネルギーを発光イオンに伝達し発光するが、長波長紫外線および短波長可視光線（350nmから420nm）の吸収は十分でない。本発明の赤色発光蛍光体は、発光イオンであるユーロピウムイオンが直接、長波長紫外線および短波長可視光線（350nmから420nm）を吸収している。このことから赤色発光強度はユーロピウム濃度に依存し、ユーロピウム濃度が最大のとき発光強度も最大となる。

【0018】しかし、一般的な蛍光体において発光イオン（付活剤）濃度は母体結晶に対し数モル%添加され、それ以上の濃度では①付活剤の間に共鳴伝達による交差緩和が生じ、励起エネルギーの一部が失われる。②付活剤間の共鳴伝達による励起の回遊が生じ、これが結晶表面や非発光中心への励起の移行と消滅を助長する。③付活剤同士が凝集あるいはイオン対を形成することによって、非発光中心やキラー（蛍光抑制剤）に変わるなどの理由によって濃度消光が起こることが知られている。

【0019】ところが、本発明の赤色発光蛍光体のような発光イオンが、1次元や2次元のように低次元に配置している化合物では、発光イオンが配列している層と層との間隔が広いため、励起エネルギーの回遊が制御されることによって濃度消光を示さない。このことからユーロピウムイオンの4f軌道内の不対電子によって長波長紫外線および短波長可視光線（350nmから420nm）を効率よく吸収し赤色発光が得られる。

【0020】また、上記の赤色発光蛍光体の発光ピークは614nmで、Y_2O_2S：Euの発光ピークより短波長側に位置している。このことから、これら2種類の蛍光体を併用することにより赤色領域の発光面積が増加されるため高輝度の白色を得ることも可能である。

【0021】

【発明の実施の形態】以下，本発明の実施の形態を、以下の実施例に基づいて説明する。

【実施例1】蛍光体構成原料として、WO_3粉末を3.96gと、Eu_2O_3粉末を1.50gと、Li_2CO_3粉末を0.32gを正確に秤量し、これをボールミルを使用して均一に混合して原料混合体とした。

【0022】次に、得られた原料混合体を、アルミナ製坩堝に入れ900℃の温度で6時間焼成した。得られた焼成物を純水にて十分洗浄し、不要な可溶成分を除去し、その後、ボールミルにより細かく粉砕し、篩い分けを行い、$LiEuW_2O_8$なる組成の赤色発光蛍光体を調製した。

【0023】そして、上記赤色発光蛍光体$LiEuW_2O_8$について380nm励起下において、従来のY_2O_2S：Eu^{3+}蛍光体を標準にして発光強度を測定したところ、図1に示すように、2.5倍という高い値が得られた。$LiEuW_2O_8$の発光ピークは614nm、Y_2O_2S：Eu^{3+}の発光ピークは624nmであることから、これらの蛍光体を併用して用いると赤領域の発光面積を増加させることができる。

【0024】また、上記赤色発光蛍光体$LiEuW_2O_8$の励起波長は、長波長紫外線および短波長可視光線（350nm～420nm）に位置していることから、この範囲の波長を614nmに変換することが可能である。特に380nmに最大吸収ピークがあるため380nm前後に発光する励起光源について有効である。

【0025】

【実施例2】赤色発光蛍光体として$LiEuW_2O_8$と、青色発光蛍光体として$Sr_5(PO_4)_3Cl$：Euと、緑色発光蛍光体として$BaMg_2Al_{16}O_{27}$：Eu，Mnとを10：3：3の割合でシリコーンゴムに混合し、これを加熱プレス機を用いて図5に示すキャップ形状に成形した。これを発光波長が380nmの紫外LEDの外側に被覆し、積分球中において20mAで点灯させた。得られた分光分布を分光放射輝度計PR－704（Photo Research製）で測色した。得られた分光分布を図3に示す。赤色蛍光体にY_2O_2S：Euを用いた場合と比較して2.3倍の輝度をもつ白色光が得られた。

【0026】

【実施例3】赤色発光蛍光体として$LiEuW_2O_8$と

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Y_2O_2S：Euを、青色発光蛍光体として$Sr_5(PO_4)_3Cl$：Euを、緑色発光蛍光体として$BaMg_2Al_{16}O_{27}$：Eu，Mnを15：15：3：3の割合でシリコーンゴムに混合し、それを加熱プレス機を用いてキャップ形状に成形した。これを発光波長が380nmの紫外LEDの外側に被覆し、積分球中において20mAで点灯させた。得られた分光分布を分光放射輝度計PR-704（Photo Research製）で測色した。得られた分光分布を図4に示す。赤色蛍光体にY_2O_2S：Euを用いた場合と比較して1．6倍の輝度をもつ白色光が得られた。

【0027】図5は、上記した実施例2及び実施例3で説明したキャップ形状の蛍光体入り被覆体を示し、具体的には、発光ダイオード1におけるモールド部材2の外側表面に、本発明に係る蛍光体をシリコーンゴムに混合し、これをキャップ形状に形成した被覆体3を被せた発光装置である。尚、蛍光体は、発光ダイオード1における発光素子4の外表面を被覆するコーティング部材に混入しても、或いはモールド部材2に混入して、更には発光ダイオードの投光方向前方に配置する透光シートに混入してもよいものである。

【0028】

【発明の効果】以上説明の通り、本発明に係る赤色発光蛍光体によれば、長波長紫外線および短波長可視光線励起で強い発光強度をもつ赤色発光が得られる。また、Eu^{3+}イオンによって励起紫外線を効率良く吸収し、発光しているため励起波長がシフトしても影響を受けにくく、安定した色調および発光強度を提供できる。

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【0029】また、本発明に係る赤色発光蛍光体と他の蛍光体を組み合わせることにより、高輝度の白色光が得られるばかりでなく安定した様々な色調を提供することができる。

【図面の簡単な説明】

【図1】本発明に係る赤色発光蛍光体（$LiEuW_2O_8$）とY_2O_2S：Eu^{3+}の発光スペクトル分布を示すグラフである。

【図2】本発明に係る赤色発光蛍光体（$LiEuW_2O_8$）の励起スペクトル分布を示すグラフである。

【図3】実施例2による発光の分光分布を示すグラフである。

【図4】実施例3による発光の分光分布を示すグラフである。

【図5】発光ダイオードにおけるモールド部材の外側に、蛍光体層を設けた発光装置を示す断面図である。

【図6】Eu^{3+}イオンが2次元に配列した化合物のモデル図である。

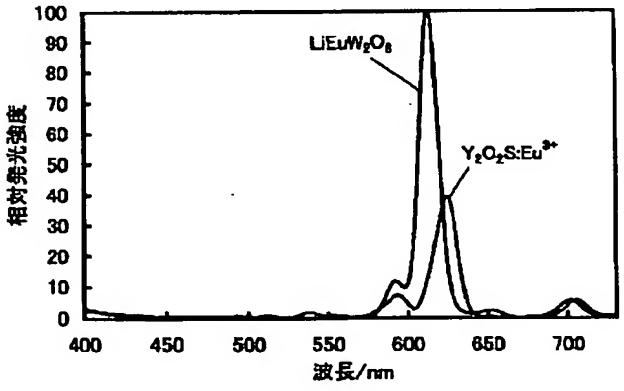
【図7】Eu^{3+}イオンが1次元に配列した化合物のモデル図である。

【符号の説明】

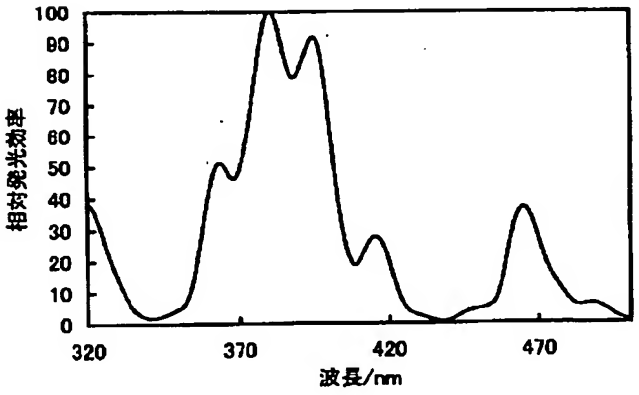
1…発光ダイオード　　2…モールド部材

3…被覆体（キャップ形状）

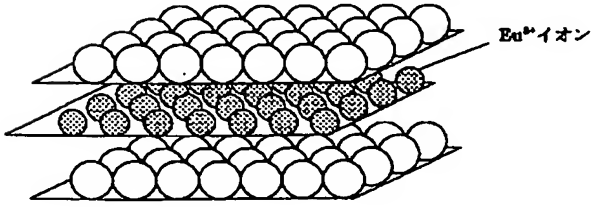
【図1】



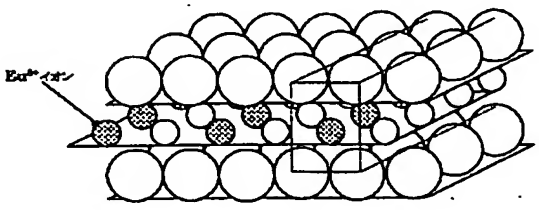
【図2】



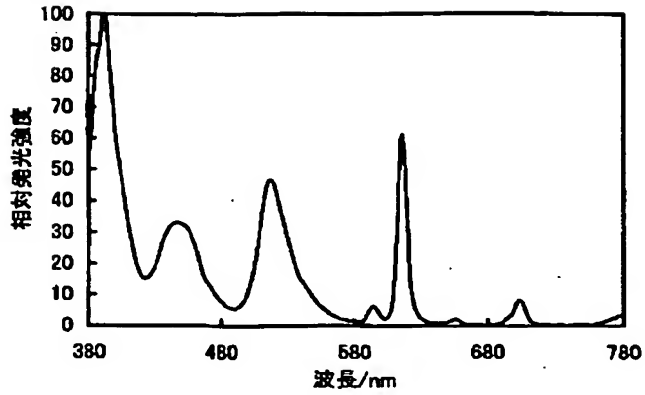
【図6】



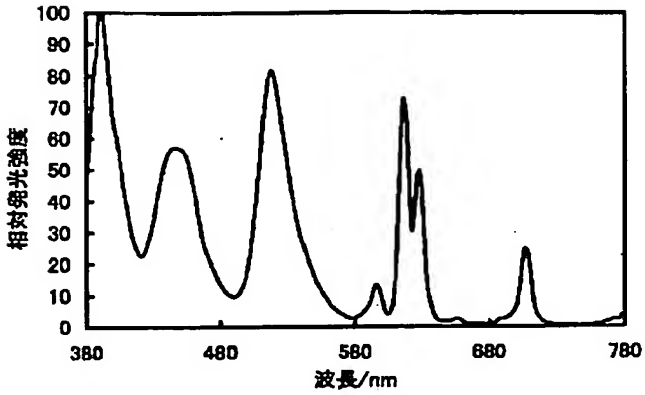
【図7】



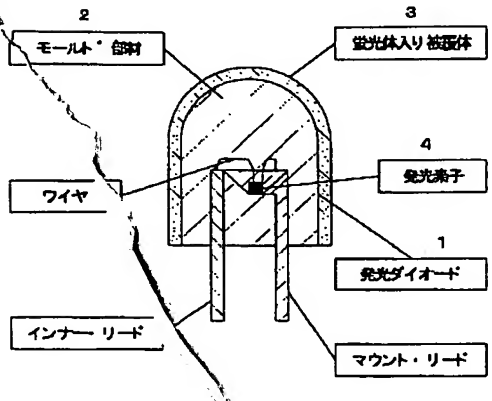
【図３】



【図４】



【図５】



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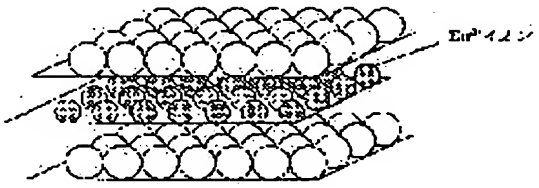
(54) RED COLOR-EMITTING PHOSPHOR AND LIGHT-EMITTING DEVICE USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a red color-emitting phosphor which efficiently radiates a red emission by a long wavelength ultraviolet ray or a short wavelength visible ray (from 350 nm to 420 nm), particularly by an exciting light having a wavelength of around 370 nm, and is practically employable for obtaining a white or an arbitrary color tone from one light-emitting diode, and an LED lamp using the phosphor.
SOLUTION: In the phosphor radiating emission by excitation by a long wavelength ultraviolet ray or a short wavelength visible ray having a light- emitting wavelength of 350 nm to 420 nm, an Eu3+ ion is arranged bidimensionally or unidimensionally.



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CLAIMS

[Claim(s)]
[Claim 1] The red luminescence fluorescent substance characterized by being the fluorescent substance which arranged Eu3+ ion to two-dimensional or one dimension in the fluorescent substance with which luminescence wavelength is excited by 350 to 420nm ultraviolet A, and the short wavelength visible ray, and emits light.
[Claim 2] The red luminescence fluorescent substance according to claim 1 characterized by expressing the presentation of the above-mentioned fluorescent substance with AEuXLn(1-X) M2O8. However, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs, Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is at least 11 sorts chosen from the group which consists of W or Mo.
[Claim 3] AEuXLn(1-X) M2O8 (however, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs, and Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu W M) or at least one sort chosen from the group which consists of Mo -- it is -- the red luminescence fluorescent substance according to claim 2 characterized by the particle diameter being 50 micrometers or less in the red luminescence fluorescent substance which has the presentation expressed.
[Claim 4] Luminescence equipment characterized by preparing a fluorescent substance layer given in any above-mentioned claim 1 thru/or] of 3 they are on the luminescence chip which emits light in 350 to 420nm ultraviolet A, and a short wavelength visible ray.
[Claim 5] Luminescence equipment according to claim 4 which consists of two or more fluorescent substance layers which the above-mentioned fluorescent substance layer turns into from a fluorescent substance according to claim 1 or 2.
[Claim 6] Luminescence equipment according to claim 4 whose above-mentioned fluorescent substance layer is the monolayer structure which mixed two or more fluorescent substances according to claim 1 or 2.
[Claim 7] Luminescence equipment characterized by distributing above-mentioned claim 1 or a fluorescent substance given in 2 to the mould member of the light emitting diode which emits light in 350 to 420nm ultraviolet A, and a short wavelength visible ray.
[Claim 8] Luminescence equipment which the mould member of the light emitting diode which emits light in 350 to 420nm ultraviolet A and a short wavelength visible ray is made to distribute two or more fluorescent substances, and is characterized by using above-mentioned claim 1 or a fluorescent substance given in 2 one of the fluorescent substance of the.
[Claim 9] Luminescence equipment characterized by preparing a fluorescent substance layer according to claim 1 or 2 in the outside of the mould member of the light emitting diode which emits light in 350 to 420nm ultraviolet A, and a short wavelength visible ray.
[Claim 10] Luminescence equipment whose one of the luminous layer of the two or more luminous layers are prepared in the outside of the mould member of the light emitting diode which emits light in 350 to 420nm ultraviolet A, and a short wavelength visible ray, and is above-mentioned claim 1 or a fluorescent substance given in 2 [claim 11] Luminescence equipment prepare the mixing layer which mixed two or more fluorescent substances in the outside of the mould member of the light emitting diode which emits light in 350 to 420nm ultraviolet A, and a short wavelength visible ray, and using the fluorescent substance given in one of the fluorescent substance of the at above-mentioned claims 1 or 2.
[Claim 12] Luminescence equipment given in claim 4 characterized by mixing at least one sort of a fluorescent substance and other red luminescence fluorescent substances given in above-mentioned claim 1 or 2 as a red luminescence fluorescent substance thru/or any 1 term of 11.
[Claim 13] Luminescence equipment which put the coat object which mixed two or more fluorescent substances on the outside of the mould member of the light emitting diode which emits light in 350 to 420nm ultraviolet A, and a short wavelength visible ray, and used the fluorescent substance according to claim 1 or 2 for it one of the fluorescent substance of the

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the fluorescent substance which is excited by 350 to 420nm ultraviolet A, and the short wavelength visible ray, and emits light in red, and the luminescence equipment using the fluorescent substance.
[0002]
[Description of the Prior Art] As a fluorescent substance excited by current, the ultraviolet A mainly used, and the short wavelength visible ray (from 350nm to 420nm) BaMg2aluminum16O27:Eu with the blue luminescent color, 5 (Sr, calcium, Ba) (PO4) 3Cl:Eu, and green BaMg2aluminum16O27: — there are Eu, Mn, Zn2GeO4:Mn, red Y2O2 S:Eu, and 3.5MgO, 0.5MgF2 and GeO2:Mn. By mixing the fluorescent substance of these 3 color at a rate of arbitration, many luminescent color can be made from ultraviolet A and a short wavelength visible ray. However, in the case of a white system, since the luminous efficiency of the Y2O2 S:Eu fluorescent substance of a red component was quite lower than other fluorescent substances, there was a problem that a mixed rate increased. Furthermore, although white could be obtained by red, green, and blue luminescence balance by the white system, since the luminous efficiency of a red component was bad, the amount of luminescence of green and a blue system fluorescent substance had to be stopped low, and the white of high brightness was not obtained.
[0003] The wavelength corresponding to the excitation energy of the electron pair of an oxide system compound is in an ultraviolet region, and ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) lap with the absorption end of a fluorescent substance. In order to solve this problem, it is reported that the rare earth oxysulfide fluorescent substance activated with europium is proposed by JP,11-246857,A or JP,2000-144130,A, and shifts excitation wavelength to a long wavelength side. However, since the luminescence wavelength ultraviolet [LED] near 370nm lapped with the absorption end of these fluorescent substances, it had the problem from which the amount of luminescence changes with the shifts of a luminescence peak ultraviolet [LED] remarkably.
[0004] On the other hand, light emitting diode (LED:Light Emitting Diode) is semiconductor diode which emits light, and changes electrical energy into the light or infrared light. In order to use especially the light, it is widely used as an LED lamp which closed the luminescence chip formed by luminescent material, such as GaP, and GaAsP, GaAlAs, by transparence resin etc. Moreover, luminescent material is fixed to the top face of a printed circuit board metallurgy group lead, and the LED lamp of the display mold closed in the resin case which imitated the figure and the alphabetic character is also used abundantly.
[0005] Moreover, it is also possible by making various kinds of fluorescent substance powder contain in the front face of a luminescence chip thru/or the resin of light emitting diode to adjust the color of synchrotron orbital radiation proper. That is, the luminescent color of an LED lamp can reproduce luminescence of a light field according to each activity application from blue to red. Moreover, since it is a semiconductor device, the life of light emitting diode is long and it is reliable, and since the exchange is relief-ized when it uses as the light source, it is widely used as a component part of various displays, such as pocket communication equipment, a personal computer peripheral device, OA equipment, a home electrical machinery and apparatus, audio equipment, various switches, the light source for back lights, and the plotting board.
[0006]
[Problem(s) to be Solved by the Invention] However, the color sense of the user of the various above-mentioned displays improves further, and recently requires the function which can reproduce a delicate hue to a high definition more also in various displays. Moreover, the function which can reproduce white thru/or various kinds of neutral colors with one light emitting diode is also called for strongly.
[0007] Therefore, white thru/or constituting so that the neutral colors of arbitration may be taken out are also tried from one light emitting diode by applying blue, red, and a green luminescence fluorescent substance to the front face of the luminescence chip of an LED lamp further, or making the various above-mentioned fluorescent substance powder contain in the resin (for example, a mould member, a coating member, etc.) which constitutes a light emitting diode.
[0008] However, the red luminescence fluorescent substance had especially ultraviolet A and a short wavelength visible ray (from 350nm to 420nm), and the trouble that absorption was weak, to the excitation light before and behind the wavelength of 370nm as compared with other blue and a green luminescence fluorescent substance. Moreover, as for the excitation wavelength of the rare earth oxysulfide fluorescent substance activated with the europium proposed, for example by red fluorescent substance Y2O2 S:Eu, JP,11-246857,A, or JP,2000-144130,A, on long wavelength, absorption intensity falls rapidly from 350nm. When the excitation light source LED which makes 350nm - 380nm a luminescence peak from this, for example, ultraviolet, is used for the excitation light source, it is difficult for the amount of red luminescence of a fluorescent substance to change with the shifts of the luminescence peak which is on ultraviolet LED manufacture and is generated remarkably, and to reproduce a delicate hue to a high definition more.
[0009] This invention is made in order to solve the above-mentioned trouble, and it aims at offering the LED lamp which used ultraviolet A and a short wavelength visible ray (from 350nm to 420nm), the red luminescence fluorescent substance that can be used practical in order [that it is white from one light emitting diode] to be, to carry out and to take out the color tone of arbitration, and its fluorescent substance by the ability emitting [as opposed to / especially / the excitation light before and behind the wavelength of 370nm] red luminescence efficiently.
[0010]
[Means for Solving the Problem] In order that this invention persons might attain the above-mentioned object, they

prepared the red luminescence fluorescent substance which consists of various presentations, and did comparison examination of the effect the class and addition of this presentation component affect excitation-spectrum distribution of a fluorescent substance and luminescence reinforcement by experiment.

[0011] Consequently, in the compound 2O8 which europium arranged into the low dimension, for example, LiEuW, it was shown clearly that ultraviolet A and a short wavelength visible ray (from 350nm to 420nm), and the red luminescence fluorescent substance that the excitation light before and behind the wavelength of 370nm is absorbed especially, and can emit red luminescence efficiently are obtained. This invention is completed based on the above-mentioned knowledge.

[0012] That is, the red luminescence fluorescent substance concerning this invention is characterized by Eu3+ ion being the fluorescent substance arranged to two-dimensional or one dimension. As it is indicated in drawing 6 as the condition that Eu3+ ion arranged to two-dimensional, the condition that Eu3+ ion is arranged by length and the longitudinal direction in the same flat surface is said, and the condition that Eu3+ ion is arranged by the lengthwise direction (or longitudinal direction) in the same flat surface as it is indicated in drawing 7 as the condition of having arranged to one dimension is said.

[0013] Furthermore, a presentation is AEuXLn(1-X) M2O8 (however, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs). Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is at least one sort chosen from the group which consists of W or Mo. It is characterized by what is expressed. Moreover, the most desirable presentation is LiEuW 2O8.

[0014] Moreover, the red luminescence fluorescent substance concerning this invention is AEuXLn(1-X) M2O8 (however, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs). Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is the presentation of being at least one sort chosen from the group which consists of W or Mo, and it is characterized by the mean particle diameter of the particle being 50 micrometers or less.

[0015] Furthermore, the luminescence equipment concerning this invention is set by energizing for the luminescence chip combined with the fluorescent substance to LED which changes electrical energy into the light or infrared light. The fluorescent substance layer prepared on the above-mentioned luminescence chip AEuXLn(1-X) M2O8 (However, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs.) Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is at least one sort chosen from the group which consists of W or Mo — it is — it is characterized by things. Here, the above-mentioned fluorescent substance layer prepared on a luminescence chip may carry out laminating arrangement of a monolayer or two or more layers at the shape of a layer, and two or more fluorescent substances may be mixed in a single layer, and it may arrange at least one or more sorts of fluorescent substances. As a gestalt which prepares a fluorescent substance layer on the above-mentioned luminescence chip, the gestalt which mixes a fluorescent substance to the coating member which covers the front face of a luminescence chip, the gestalt which mixes a fluorescent substance to a mould member or the gestalt which mixes a fluorescent substance on the coat object put on a mould member, the gestalt which arrange the plate which mixed the fluorescent substance ahead [of an LED lamp / floodlighting side], and in which light transmission is possible are mentioned further.

[0016] Moreover, the above-mentioned fluorescent substance may add at least one or more sorts of fluorescent substances to the mould member on a luminescence chip. Furthermore, one or more sorts of fluorescent substance layers of the above-mentioned fluorescent substance may be prepared in the outside of light emitting diode. As a gestalt prepared in the outside of light emitting diode, the gestalt which applies a fluorescent substance to the outside front face of the mould member of light emitting diode in the shape of a layer, or the Plastic solid (the shape of for example, a cap) which made rubber, resin, an elastomer, etc. distribute a fluorescent substance is created, the gestalt which covers this to LED, or said Plastic solid is processed into plate-like, and the gestalt which arranges this ahead of LED is mentioned.

[0017] Here, in the above-mentioned red luminescence fluorescent substance, europium acts as the excitation absorption of light and an emission center. In a common oxide system fluorescent substance, the wavelength corresponding to the excitation energy of an electron pair is in an ultraviolet region. Although excitation light is absorbed with host crystal, the excitation energy is transmitted to luminescence ion and light is emitted, absorption of ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) is not enough. The europium ion whose red luminescence fluorescent substance of this invention is luminescence ion is absorbing ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) directly. When europium concentration is max depending on europium concentration, as for red luminescence reinforcement, luminescence reinforcement also serves as max from this.

[0018] however, a common fluorescent substance — setting — luminescence ion (activator) concentration — host crystal — receiving — several mol % — it is added, and by the concentration beyond it, between ** activators, the cross relaxation by resonance transfer arises and a part of excitation energy is lost. ** Migration of excitation by the resonance transfer between activators arises, and this promotes shift and dissipation of the excitation to a crystal front face or a nonluminescent core. ** When activators form condensation or an ion pair, it is known that concentration quenching will happen for the reasons of changing to a nonluminescent core or a killer (fluorescence inhibitor).

[0019] However, with the compound which luminescence ion like the red luminescence fluorescent substance of this invention arranges into the low dimension like one dimension or two-dimensional, since spacing of the layer and layer which luminescence ion has arranged is large, concentration quenching is not shown by controlling migration of excitation energy. Ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) are efficiently absorbed with the unpaired electron within 4f orbit of europium ion from this, and red luminescence is obtained.

[0020] Moreover, the luminescence peak of the above-mentioned red luminescence fluorescent substance is 614nm, and is located in a short wavelength side from the luminescence peak of Y2O2 S:Eu. Since the luminescence area of a red field is increased from this by using together these two kinds of fluorescent substances, it is also possible to obtain the white of high brightness.

[0021]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained based on the following examples.

[Example 1] as a fluorescent substance configuration raw material — WO3 powder — 3.96g and 2OEu3 powder — 1.50g and Li2CO3 powder — 0.32g — accuracy — weighing capacity — carrying out — this — a ball mill — using it —

homogeneity — mixing — a raw material — it considered as the mixture.
[0022] next, the obtained raw material — the mixture was put into the crucible made from an alumina, and was calcinated at the temperature of 900 degrees C for 6 hours. Pure water washed the obtained baking object enough, and the unnecessary meltable component was removed, and the ball mill ground finely after that, it sifted out, and the red luminescence fluorescent substance of the presentation which becomes LiEuW2O8 was prepared.
[0023] And when the conventional Y2O2 S:Eu3+ fluorescent substance was made into the criterion under 380nm excitation about the above-mentioned red luminescence fluorescent substance LiEuW 2O8 and luminescence reinforcement was measured, as shown in drawing 1 , the high value of 2.5 times was acquired. The luminescence peak of LiEuW 2O8 can make the luminescence area of a red field increase, since the luminescence peak of 614nm and Y2O2 S:Eu3+ is 624nm, if these fluorescent substances are used together and used.
[0024] Moreover, since the excitation wavelength of the above-mentioned red luminescence fluorescent substance LiEuW 2O8 is located in ultraviolet A and a short wavelength visible ray (350nm - 420nm), it can change the wavelength of this range into 614nm. Since the maximum absorption peak is especially in 380nm, it is effective about the excitation light source which emits light before and after 380nm.
[0025]
[Example 2] as a red luminescence fluorescent substance — as LiEuW 2O8 and a blue luminescence fluorescent substance — as Sr5 (PO4) 3Cl:Eu and a green luminescence fluorescent substance — BaMg2aluminum16O27: — Mn was mixed to silicone rubber at a rate of Eu and10:3:3, and this was fabricated in the cap configuration shown in drawing 5 using a hot press machine. This was covered on the outside ultraviolet [LED] whose luminescence wavelength is 380nm, and the light was made to switch on by 20mA in an integrating sphere. The colorimetry of the acquired spectral distribution was carried out by spectral radiance meter—704 (product made from Photo Research). The acquired spectral distribution are shown in drawing 3. The white light which has one 2.3 times the brightness of this in a red fluorescent substance as compared with the case where Y2O2 S:Eu is used was acquired.
[0026]
[Example 3] as a red luminescence fluorescent substance — LiEuW 2O8 and Y2O2 S:Eu — as a blue luminescence fluorescent substance — Sr5 (PO4) 3Cl:Eu — as a green luminescence fluorescent substance — BaMg2aluminum16O27: — Mn was mixed to silicone rubber at a rate of Eu and15:15:3:3, and it was fabricated in the cap configuration using the hot press machine. This was covered on the outside ultraviolet [LED] whose luminescence wavelength is 380nm, and the light was made to switch on by 20mA in an integrating sphere. The colorimetry of the acquired spectral distribution was carried out by spectral radiance meter—704 (product made from Photo Research). The acquired spectral distribution are shown in drawing 4. The white light which has one 1.6 times the brightness of this in a red fluorescent substance as compared with the case where Y2O2 S:Eu is used was acquired.
[0027] Drawing 5 is luminescence equipment on which the coat object 3 which showed the coat object containing a fluorescent substance of a cap configuration explained in the above-mentioned example 2 and the above-mentioned example 3, specifically mixed the fluorescent substance applied to this invention on the outside front face of the mould member 2 in light emitting diode 1 to silicone rubber, and formed this in the cap configuration was put. In addition, it may mix in the mould member 2 and a fluorescent substance may be mixed in the translucent sheet arranged further ahead [of a light emitting diode / floodlighting direction], even if it mixes in the coating member which covers the outside surface of the light emitting device 4 in a light emitting diode 1.
[0028]
[Effect of the Invention] According to the red luminescence fluorescent substance applied to this invention above as explanation, red luminescence with strong luminescence reinforcement is obtained by ultraviolet A and short wavelength visible-ray excitation. Moreover, since excitation ultraviolet rays are absorbed efficiently and light is emitted with Eu3+ ion, even if excitation wavelength shifts, it is hard to be influenced and the stable color tone and luminescence reinforcement can be offered.
[0029] Moreover, various color tones the white light of high brightness is not only acquired, but stabilized can be offered by combining the red luminescence fluorescent substance concerning this invention, and other fluorescent substances.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the fluorescent substance which is excited by 350 to 420nm ultraviolet A, and the short wavelength visible ray, and emits light in red, and the luminescence equipment using the fluorescent substance.

[Translation done.]

PRIOR ART

[Description of the Prior Art] As a fluorescent substance excited by current, the ultraviolet A mainly used, and the short wavelength visible ray (from 350nm to 420nm) BaMg2aluminum16O27:Eu with the blue luminescent color, 5 (Sr, calcium, Ba) (PO4) 3Cl:Eu, and green BaMg2aluminum16O27: — there are Eu, Mn, Zn2GeO4:Mn, red Y2O2 S:Eu, and 3.5MgO, 0.5MgF2 and GeO2:Mn. By mixing the fluorescent substance of these 3 color at a rate of arbitration, many luminescent color can be made from ultraviolet A and a short wavelength visible ray. However, in the case of a white system, since the luminous efficiency of the Y2O2 S:Eu fluorescent substance of a red component was quite lower than other fluorescent substances, there was a problem that a mixed rate increased. Furthermore, although white could be obtained by red, green, and blue luminescence balance by the white system, since the luminous efficiency of a red component was bad, the amount of luminescence of green and a blue system fluorescent substance had to be stopped low, and the white of high brightness was not obtained.

[0003] The wavelength corresponding to the excitation energy of the electron pair of an oxide system compound is in an ultraviolet region, and ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) lap with the absorption end of a fluorescent substance. In order to solve this problem, it is reported that the rare earth oxysulfide fluorescent substance activated with europium is proposed by JP,11-246857,A or JP,2000-144130,A, and shifts excitation wavelength to a long wavelength side. However, since the luminescence wavelength ultraviolet [LED] near 370nm lapped with the absorption end of these fluorescent substances, it had the problem from which the amount of luminescence changes with the shifts of a luminescence peak ultraviolet [LED] remarkably.

[0004] On the other hand, light emitting diode (LED:Light Emitting Diode) is semiconductor diode which emits light, and changes electrical energy into the light or infrared light. In order to use especially the light, it is widely used as an LED lamp which closed the luminescence chip formed by luminescent material, such as GaP, and GaAsP, GaAlAs, by transparence resin etc. Moreover, luminescent material is fixed to the top face of a printed circuit board metallurgy group lead, and the LED lamp of the display mold closed in the resin case which imitated the figure and the alphabetic character is also used abundantly.

[0005] Moreover, it is also possible by making various kinds of fluorescent substance powder contain in the front face of a luminescence chip thru/or the resin of light emitting diode to adjust the color of synchrotron orbital radiation proper. That is, the luminescent color of an LED lamp can reproduce luminescence of a light field according to each activity application from blue to red. Moreover, since it is a semiconductor device, the life of light emitting diode is long and it is reliable, and since the exchange is relief-ized when it uses as the light source, it is widely used as a component part of various displays, such as pocket communication equipment, a personal computer peripheral device, OA equipment, a home electrical machinery and apparatus, audio equipment, various switches, the light source for back lights, and the plotting board.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to the red luminescence fluorescent substance applied to this invention above as explanation, red luminescence with strong luminescence reinforcement is obtained by ultraviolet A and short wavelength visible-ray excitation. Moreover, since excitation ultraviolet rays are absorbed efficiently and light is emitted with Eu3+ ion, even if excitation wavelength shifts, it is hard to be influenced and the stable color tone and luminescence reinforcement can be offered.
[0029] Moreover, various color tones the white light of high brightness is not only acquired, but stabilized can be offered by combining the red luminescence fluorescent substance concerning this invention, and other fluorescent substances.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, the color sense of the user of the various above-mentioned displays improves further, and recently requires the function which can reproduce a delicate hue to a high definition more also in various displays. Moreover, the function which can reproduce white thru/or various kinds of neutral colors with one light emitting diode is also called for strongly.
[0007] Therefore, white thru/or constituting so that the neutral colors of arbitration may be taken out are also tried from one light emitting diode by applying blue, red, and a green luminescence fluorescent substance to the front face of the luminescence chip of an LED lamp further, or making the various above-mentioned fluorescent substance powder contain in the resin (for example, a mould member, a coating member, etc.) which constitutes a light emitting diode.
[0008] However, the red luminescence fluorescent substance had especially ultraviolet A and a short wavelength visible ray (from 350nm to 420nm), and the trouble that absorption was weak, to the excitation light before and behind the wavelength of 370nm as compared with other blue and a green luminescence fluorescent substance. Moreover, as for the excitation wavelength of the rare earth oxysulfide fluorescent substance activated with the europium proposed, for example by red fluorescent substance Y2O2 S:Eu, JP,11-246857,A, or JP,2000-144130,A, on long wavelength, absorption intensity falls rapidly from 350nm. When the excitation light source LED which makes 350nm - 380nm a luminescence peak from this, for example, ultraviolet, is used for the excitation light source, it is difficult for the amount of red luminescence of a fluorescent substance to change with the shifts of the luminescence peak which is on ultraviolet LED manufacture and is generated remarkably, and to reproduce a delicate hue to a high definition more.
[0009] This invention is made in order to solve the above-mentioned trouble, and it aims at offering the LED lamp which used ultraviolet A and a short wavelength visible ray (from 350nm to 420nm), the red luminescence fluorescent substance that can be used practical in order [that it is white from one light emitting diode] to be, to carry out and to take out the color tone of arbitration, and its fluorescent substance by the ability emitting [as opposed to / especially / the excitation light before and behind the wavelength of 370nm] red luminescence efficiently.

[Translation done.]

MEANS

[Means for Solving the Problem] In order that this invention persons might attain the above-mentioned object, they prepared the red luminescence fluorescent substance which consists of various presentations, and did comparison examination of the effect the class and addition of this presentation component affect excitation-spectrum distribution of a fluorescent substance and luminescence reinforcement by experiment.
[0011] Consequently, in the compound 2O8 which europium arranged into the low dimension, for example, LiEuW, it was shown clearly that ultraviolet A and a short wavelength visible ray (from 350nm to 420nm), and the red luminescence fluorescent substance that the excitation light before and behind the wavelength of 370nm is absorbed especially, and can emit red luminescence efficiently are obtained. This invention is completed based on the above-mentioned knowledge.
[0012] That is, the red luminescence fluorescent substance concerning this invention is characterized by Eu3+ ion being the fluorescent substance arranged to two-dimensional or one dimension. As it is indicated in drawing 6 as the condition that Eu3+ ion arranged to two-dimensional, the condition that Eu3+ ion is arranged by length and the longitudinal direction in the same flat surface is said, and the condition that Eu3+ ion is arranged by the lengthwise direction (or longitudinal direction) in the same flat surface as it is indicated in drawing 7 as the condition of having arranged to one dimension is said.
[0013] Furthermore, a presentation is AEuXLn(1-X) M2O8 (however, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs). Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is at least one sort chosen from the group which consists of W or Mo. It is characterized by what is expressed. Moreover, the most desirable presentation is LiEuW 2O8.
[0014] Moreover, the red luminescence fluorescent substance concerning this invention is AEuXLn(1-X) M2O8 (however, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs). Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is the presentation of being at least one sort chosen from the group which consists of W or Mo, and it is characterized by the mean particle diameter of the particle being 50 micrometers or less.
[0015] Furthermore, the luminescence equipment concerning this invention is set by energizing for the luminescence chip combined with the fluorescent substance to LED which changes electrical energy into the light or infrared light. The fluorescent substance layer prepared on the above-mentioned luminescence chip AEuXLn(1-X) M2O8 (However, A under 0< x<=1 and presentation is at least one sort chosen from the group which consists of Li, Na, K, Rb, and Cs.) Ln is at least one chosen from the group which consists of Y, La, Gd, and Lu, and M is at least one sort chosen from the group which consists of W or Mo — it is — it is characterized by things. Here, the above-mentioned fluorescent substance layer prepared on a luminescence chip may carry out laminating arrangement of a monolayer or two or more layers at the shape of a layer, and two or more fluorescent substances may be mixed in a single layer, and it may arrange at least one or more sorts of fluorescent substances. As a gestalt which prepares a fluorescent substance layer on the above-mentioned luminescence chip, the gestalt which mixes a fluorescent substance to the coating member which covers the front face of a luminescence chip, the gestalt which mixes a fluorescent substance to a mould member or the gestalt which mixes a fluorescent substance on the coat object put on a mould member, the gestalt which arrange the plate which mixed the fluorescent substance ahead [of an LED lamp / floodlighting side], and in which light transmission is possible are mentioned further.
[0016] Moreover, the above-mentioned fluorescent substance may add at least one or more sorts of fluorescent substances to the mould member on a luminescence chip. Furthermore, one or more sorts of fluorescent substance layers of the above-mentioned fluorescent substance may be prepared in the outside of light emitting diode. As a gestalt prepared in the outside of light emitting diode, the gestalt which applies a fluorescent substance to the outside front face of the mould member of light emitting diode in the shape of a layer, or the Plastic solid (the shape of for example, a cap) which made rubber, resin, an elastomer, etc. distribute a fluorescent substance is created, the gestalt which covers this to LED, or said Plastic solid is processed into plate-like, and the gestalt which arranges this ahead of LED is mentioned.
[0017] Here, in the above-mentioned red luminescence fluorescent substance, europium acts as the excitation absorption of light and an emission center. In a common oxide system fluorescent substance, the wavelength corresponding to the excitation energy of an electron pair is in an ultraviolet region. Although excitation light is absorbed with host crystal, the excitation energy is transmitted to luminescence ion and light is emitted, absorption of ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) is not enough. The europium ion whose red luminescence fluorescent substance of this invention is luminescence ion is absorbing ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) directly. When europium concentration is max depending on europium concentration, as for red luminescence reinforcement, luminescence reinforcement also serves as max from this.
[0018] however, a common fluorescent substance -- setting — luminescence ion (activator) concentration — host crystal — receiving — several mol % — it is added, and by the concentration beyond it, between ** activators, the cross relaxation by resonance transfer arises and a part of excitation energy is lost. ** Migration of excitation by the resonance transfer between activators arises, and this promotes shift and dissipation of the excitation to a crystal front face or a nonluminescent core. ** When activators form condensation or an ion pair, it is known that concentration quenching will happen for the reasons of changing to a nonluminescent core or a killer (fluorescence inhibitor).
[0019] However, with the compound which luminescence ion like the red luminescence fluorescent substance of this

invention arranges into the low dimension like one dimension or two-dimensional, since spacing of the layer and layer which luminescence ion has arranged is large, concentration quenching is not shown by controlling migration of excitation energy. Ultraviolet A and a short wavelength visible ray (from 350nm to 420nm) are efficiently absorbed with the unpaired electron within 4f orbit of europium ion from this, and red luminescence is obtained.

[0020] Moreover, the luminescence peak of the above-mentioned red luminescence fluorescent substance is 614nm, and is located in a short wavelength side from the luminescence peak of Y2O2 S:Eu. Since the luminescence area of a red field is increased from this by using together these two kinds of fluorescent substances, it is also possible to obtain the white of high brightness.

[0021]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained based on the following examples.

[Example 1] as a fluorescent substance configuration raw material — WO3 powder — 3.96g and 2OEu3 powder — 1.50g and Li2CO3 powder — 0.32g — accuracy — weighing capacity — carrying out — this — a ball mill — using it — homogeneity — mixing — a raw material — it considered as the mixture.

[0022] next, the obtained raw material — the mixture was put into the crucible made from an alumina, and was calcinated at the temperature of 900 degrees C for 6 hours. Pure water washed the obtained baking object enough, and the unnecessary meltable component was removed, and the ball mill ground finely after that, it sifted out, and the red luminescence fluorescent substance of the presentation which becomes LiEuW2O8 was prepared.

[0023] And when the conventional Y2O2 S:Eu3+ fluorescent substance was made into the criterion under 380nm excitation about the above-mentioned red luminescence fluorescent substance LiEuW 2O8 and luminescence reinforcement was measured, as shown in drawing 1 , the high value of 2.5 times was acquired. The luminescence peak of LiEuW 2O8 can make the luminescence area of a red field increase, since the luminescence peak of 614nm and Y2O2 S:Eu3+ is 624nm, if these fluorescent substances are used together and used.

[0024] Moreover, since the excitation wavelength of the above-mentioned red luminescence fluorescent substance LiEuW 2O8 is located in ultraviolet A and a short wavelength visible ray (350nm - 420nm), it can change the wavelength of this range into 614nm. Since the maximum absorption peak is especially in 380nm, it is effective about the excitation light source which emits light before and after 380nm.

[0025]

[Example 2] as a red luminescence fluorescent substance — as LiEuW 2O8 and a blue luminescence fluorescent substance — as Sr5 (PO4) 3Cl:Eu and a green luminescence fluorescent substance — BaMg2aluminum16O27: — Mn was mixed to silicone rubber at a rate of Eu and10:3:3, and this was fabricated in the cap configuration shown in drawing 5 using a hot press machine. This was covered on the outside ultraviolet [LED] whose luminescence wavelength is 380nm, and the light was made to switch on by 20mA in an integrating sphere. The colorimetry of the acquired spectral distribution was carried out by spectral radiance meter—704 (product made from Photo Research). The acquired spectral distribution are shown in drawing 3. The white light which has one 2.3 times the brightness of this in a red fluorescent substance as compared with the case where Y2O2 S:Eu is used was acquired.

[0026]

[Example 3] as a red luminescence fluorescent substance — LiEuW 2O8 and Y2O2 S:Eu — as a blue luminescence fluorescent substance — Sr5 (PO4) 3Cl:Eu — as a green luminescence fluorescent substance — BaMg2aluminum16O27: — Mn was mixed to silicone rubber at a rate of Eu and15:15:3:3, and it was fabricated in the cap configuration using the hot press machine. This was covered on the outside ultraviolet [LED] whose luminescence wavelength is 380nm, and the light was made to switch on by 20mA in an integrating sphere. The colorimetry of the acquired spectral distribution was carried out by spectral radiance meter—704 (product made from Photo Research). The acquired spectral distribution are shown in drawing 4. The white light which has one 1.6 times the brightness of this in a red fluorescent substance as compared with the case where Y2O2 S:Eu is used was acquired.

[0027] Drawing 5 is luminescence equipment on which the coat object 3 which showed the coat object containing a fluorescent substance of a cap configuration explained in the above-mentioned example 2 and the above-mentioned example 3, specifically mixed the fluorescent substance applied to this invention on the outside front face of the mould member 2 in light emitting diode 1 to silicone rubber, and formed this in the cap configuration was put. In addition, it may mix in the mould member 2 and a fluorescent substance may be mixed in the translucent sheet arranged further ahead [of a light emitting diode / floodlighting direction], even if it mixes in the coating member which covers the outside surface of the light emitting device 4 in a light emitting diode 1.

[Translation done.]

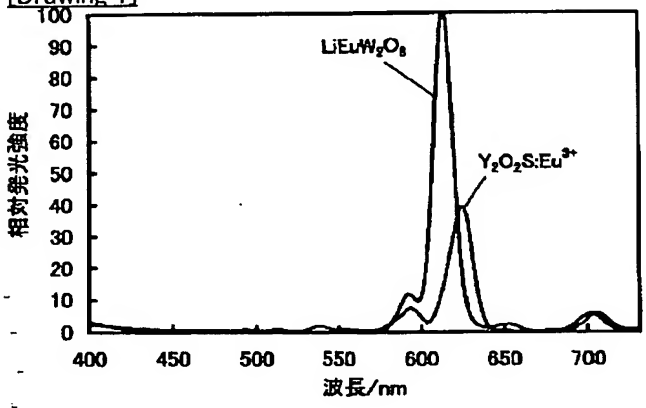
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which shows the emission spectrum distribution of a red luminescence fluorescent substance (LiEuW 2O8) and Y2O2 S:Eu3+ concerning this invention.
[Drawing 2] It is the graph which shows excitation-spectrum distribution of the red luminescence fluorescent substance (LiEuW 2O8) concerning this invention.
[Drawing 3] It is the graph which shows the spectral distribution of luminescence by the example 2.
[Drawing 4] It is the graph which shows the spectral distribution of luminescence by the example 3.
[Drawing 5] It is the sectional view showing the luminescence equipment which prepared the fluorescent substance layer in the outside of the mould member in light emitting diode.
[Drawing 6] Eu3+ ion is model drawing of the compound arranged to two-dimensional.
[Drawing 7] Eu3+ ion is model drawing of the compound arranged to one dimension.
[Description of Notations]
1 — Light emitting diode 2 — Mould member
3 — Coat object (cap configuration)

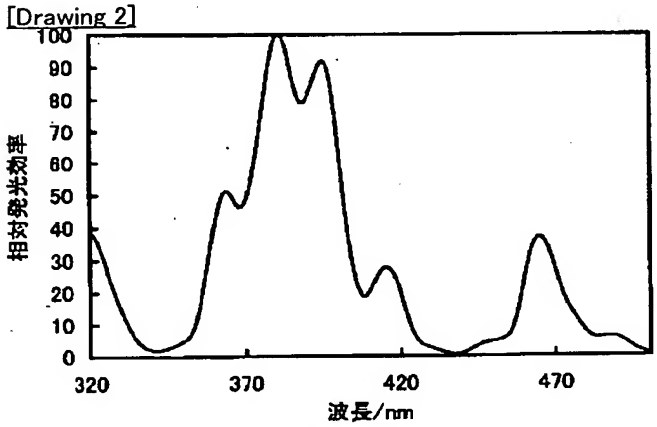
[Translation done.]

DRAWINGS

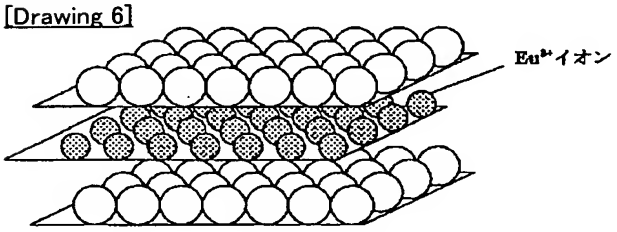
[Drawing 1]



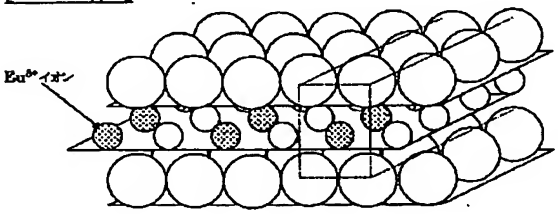
[Drawing 2]



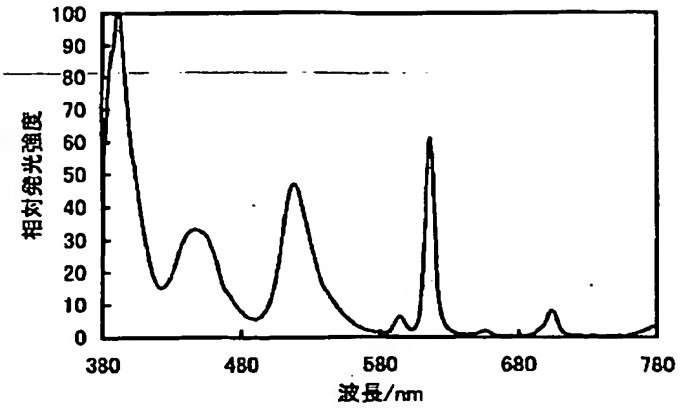
[Drawing 6]



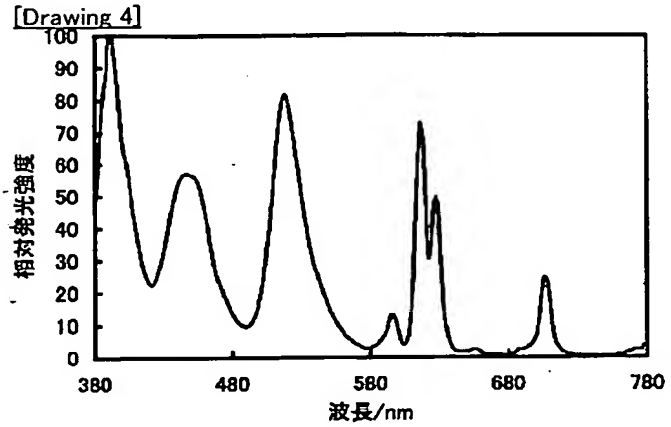
[Drawing 7]



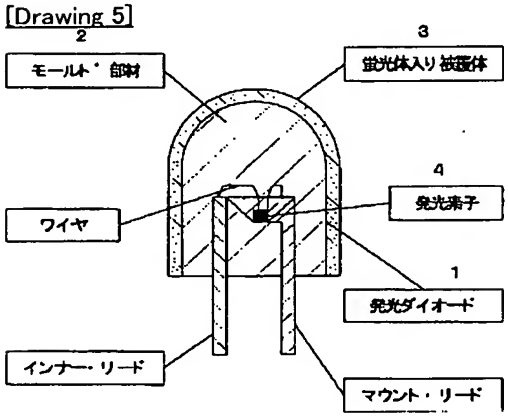
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]